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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the binder for electric double layer capacitor electrodes.

[0002]

[Description of the Prior Art] Demand has expanded the electric double layer capacitor as a backup power supply of a personal computer or a portable device. Furthermore, the upgrade is demanded as auxiliary power, such as making not only the mere object for memory backup but a size motor drive in recent years etc. In order to make an electric double layer capacitor upgrade, it is SUBJECT how a high-density electrode is developed by stopping internal resistance low. As an electrode of an electric double layer capacitor, although activated carbon is mainly used, in order to make a charge collector maintain activated carbon, activated carbon and a binder are mixed and, usually it is used. A polytetrafluoroethylene system polymer, phenol resin, an acrylic resin, cellulose, polyvinyl alcohol, water glass, etc. were used for the conventional binder for electric double layer capacitor electrodes.

[0003]

[Problem to be solved by the invention] However, when a polytetrafluoroethylene system polymer, phenol resin, cellulose, water glass, etc. are used as a binder, since the pliability of the electrode obtained is inferior, a binding property with a charge collector is not enough, and when an acrylic resin and polyvinyl alcohol are used, since resin covers the activated carbon surface or it is easy to dissolve resin itself in an electrolysis solution, there is a problem that activated carbon and a charge collector are unmaintainable. The electric double layer capacity of the electric double layer capacitor which resistance of the electrode obtained becomes high, therefore is obtained from the above point becomes low. The purpose of this invention is to provide the binder for electric double layer capacitor electrodes which it is rare to cover the activated carbon surface, and can produce the activated carbon electrode which activated carbon bound strongly to the charge collector, and attains high capacity-ization of an electric double layer capacitor, i.e., the improvement in the discharge current characteristic, by this.

[0004]

[A means for solving invention] In order that this invention may solve above-mentioned SUBJECT, (a) aromatic vinyl unit, (b) A binder for electric double layer capacitor electrodes being copolymer latex (henceforth a "specific copolymer") containing a conjugated diene unit, (c) (meta) acrylic ester unit, and (d) ethylenic-unsaturated-carboxylic-acid unit is provided. A diameter of a latex particle of the above-mentioned binder for electric double layers is a binder for characterizing [120-600 nm and a glass transition point]-by -15-150 ** electric double layer capacitor electrodes.

[0005]

[Mode for carrying out the invention] This invention is

explained in detail below. In this invention, a "unit" shows structure of each monomer origin after a monomer carries out a radical polymerization.

A specific copolymer used for <specific copolymer> this invention is a copolymer which consists of (a) aromatic vinyl unit, (b) conjugated diene unit, a (c) (meta) acrylic ester unit, and a (d) ethylenic-unsaturated-carboxylic-acid unit.

Although structure after aromatic vinyl compounds, such as styrene, alpha-methylstyrene, p-methylstyrene, vinyltoluene, KURORU styrene, and divinylbenzene, carry out a radical polymerization, for example is mentioned as an above-mentioned

(a) aromatic vinyl unit, especially being used preferably is styrene. a rate of this (a) aromatic vinyl unit -- usually -- 20- of the whole specific copolymer -- it is 40 to 75 weight % still more preferably 30 to 80weight % preferably 90weight %. In less than 20 weight %, if a copolymer may be sticky, intensity may be lost and it exceeds 90 weight %, it may be said that a copolymer becomes hard too much and bond strength as a binder and pliability are inferior. Above-mentioned (b) conjugated diene unit is an indispensable ingredient in order to give moderate pliability and elongation to a specific copolymer obtained. Structure after conjugated diene compounds, such as 1,3-butadiene, isoprene, the 2-chloro- 1, 3-butadiene, and chloroprene, carry out a radical polymerization, for example is specifically mentioned, and especially being used preferably is 1,3-butadiene. this -- (-- b --) -- conjugated diene -- a unit -- a rate -- desirable -- specific -- a copolymer -- the whole -- 40 -- weight % -- less than -- further -- desirable -- 38 -- weight % -- less than -- it is . In 40 weight % or more, a specific copolymer covers activated carbon too much, and the electric double layer capacitor characteristic may be worsened.

As an above-mentioned (c) (meta) acrylic ester unit, For example (meta), methyl acrylate, ethyl acrylate (meta), acrylic acid (meta) n-propyl, (Meta) Acrylic acid i-propyl, acrylic acid (meta) n-butyl, (Meta) Acrylic acid i-butyl, acrylic acid (meta) n-amyl, acrylic acid (meta) i-amyl, (Meta) Acrylic acid

hexyl, acrylic acid (meta) 2-hexyl, acrylic acid (meta) octyl, (Meta) Acrylic acid i-nonyl, decyl acrylate (meta), acrylic acid (meta) hydroxymethyl, (Meta) Structure after acrylic ester (meta), such as acrylic acid hydroxyethyl and acrylic acid (meta) ethylene GURIKORUJI, carries out a radical polymerization is mentioned. It is methyl acrylate (meta) methyl acrylate (meta), butyl acrylate (meta), and to especially be used preferably being used preferably. a rate of this (c) (meta-) acrylic ester unit -- 10% of the whole specific copolymer -- it is 12 to 35 weight % preferably 40weight %. In less than 10 weight %, when a constituent for electric double layer capacitor electrodes is adjusted using a binder obtained and it applies to current collection material, elasticity and intensity of a coat are inferior and it is not desirable. When it exceeds 40 weight %, the stability of a polymerization system of a specific copolymer is inferior, and adhesion as a binder, etc. fall, and it is not desirable.

[0006]

As an above-mentioned (d) ethylenic-unsaturated-carboxylic-acid unit, structure after acrylic acid, acrylic acid (meta), itaconic acid, fumaric acid, maleic acid, etc. carry out a radical polymerization is mentioned. A rate of this (d) ethylenic-unsaturated-carboxylic-acid unit is 0.1 to 10weight % of a specific copolymer preferably. In less than 0.1 weight %, if binder performance of a copolymer and chemical resistance may be inferior and it exceeds 10 weight % on the other hand, it may become that in which a water resisting property and storage stability are inferior. In a specific copolymer used in this invention, a functional group content compound unit of (e) above-mentioned (a) - (d) and copolymerizable others may contain. As an above-mentioned (d) functional group content compound unit, acrylamide (meta), Alkylamide of ethylenic unsaturated carboxylic acid, such as N-methylolacrylamide; Vinyl acetate, Carboxylic acid vinyl

ester, such as vinyl propionate; Ethylenic unsaturated dicarboxylic acid, An acid anhydride, monoalkyl Astel, and monoamide; Aminoethyl acrylate, Amino alkyl ester of ethylenic unsaturated carboxylic acid, such as dimethylamino ethyl acrylate and butylamino ethyl acrylate; Aminoethyl acrylamide, Amino alkylamide of ethylenic unsaturated carboxylic acid, such as dimethyl aminomethyl methacrylamide and methylaminopropyl methacrylamide; (meta) Acrylonitrile, Vinyl cyanide system compounds, such as alpha-KURORU acrylonitrile; structure after unsaturation aliphatic series glycidyl ester, such as glycidyl (meta) acrylate, etc. carry out a radical polymerization is mentioned, and ethylenic-unsaturated-carboxylic-acid amino alkylamide is used preferably. A rate of this (e) functional group content compound unit is 0.1 to 10 weight % of the whole specific polymer preferably. These (a) Each monomer which constitutes a copolymerization unit of - (e) is one-sort independent, or two or more sorts can be used together and used for it. Glass transition points (Tg) of a specific copolymer used in this invention are usually -15 ** - 150 **, and are 5 ** - 60 ** still more preferably -5 ** - 100 ** preferably. In Tg, less than [-15 **], a copolymer covers activated carbon too much, and impedance becomes high easily. If Tg exceeds 150 **, pliability and adhesiveness may become scarce and an adhesive property to current collection material of an electrode or the moldability of an electrode may be inferior in a binder obtained with a specific copolymer.

[0007]

In this invention, when specific copolymers are the particles of core shell structure, (a-1) 5 to 75 weight % of aromatic vinyl units, 15 to 65 weight % of conjugated diene (b-1) units, (c-1) 11 to 40 weight % of acrylic ester units, 0 to 2 weight % of ethylenic-unsaturated-carboxylic-acid (d-1) units and (e-1) the above (a-1), 0 to 2 weight % (however) of functional group content compound units (meta) of a monomer - (d-1) copolymerizable others The copolymer X5 - 90 weight sections,

and (a-2) 25 to 90 weight % of aromatic vinyl units which consist of (a-1)+(b-1)+(c-1)+(d-1)+(e-1) =100 weight %, (b-2) 35 or less weight % of conjugated diene units and 11 to 40 weight % of acrylic ester (meta-(c-2)) units, (d-2) 0.5 to 30 weight % of ethylenic-unsaturated-carboxylic-acid units and (e-2) the above (a-2), 0 to 30 weight % of functional group content compound units of a monomer - (d-2) copolymerizable others. Especially the thing consisted of the copolymer Y10 which consists of (however, (a-2)+(b-2)+(c-2)+(d-2)+(e-2) =100 weight %) - 95 weight sections (however, X+Y=100 weight section) is preferred. However, when using the specific copolymer of the above-mentioned structure, the rate in the whole copolymer of each monomeric unit shows the rate in the whole particle which set the copolymer X and the copolymer Y.

[0008]

As an aromatic vinyl unit in the above-mentioned copolymer X portion (a-1), the same thing as above-mentioned (a) aromatic vinyl unit is mentioned. The rate in the copolymer X of this (a-1) aromatic vinyl unit is 25 to 45 weight % preferably five to 75weight %. At less than 5 weight %, if the intensity of the binder obtained may become insufficient and exceeds 75 weight %, a copolymer may become hard too much and the bond strength to activated carbon, a charge collector, etc. and the pliability of a binder acquired may be inferior. As the above-mentioned (b-1) conjugated diene monomeric unit, the same thing as above-mentioned (b) conjugated diene unit is mentioned. The rate in the copolymer X of this (b-1) conjugated diene unit is 25 to 45 weight % preferably 15 to 65weight %. At less than 15 weight %, a copolymer may become hard too much, the bond strength to activated carbon, a charge collector, etc. and the pliability of a binder acquired may be inferior, and when it exceeded 65 weight %, and Tg becomes low too much, prepares the constituent for electrodes and applies to current collection material, a coat becomes the sticky thing with a tack. As the above-mentioned (c-1) (meta) acrylic ester unit, the same thing

as above-mentioned (c) (meta) acrylic ester unit is mentioned. The rate in the copolymer X of this (c-1) (meta) acrylic ester unit is 20 to 35 weight % preferably ten to 40weight %. In less than 10 weight %, when the constituent for electric double layer capacitor electrodes is prepared using the binder obtained and it applies to current collection material, the elasticity and intensity of a coat are inferior and it is not desirable. When it exceeds 40 weight %, the stability of the polymerization system of a specific copolymer is inferior, and the adhesion as a binder, etc. fall, and it is not desirable. As the above-mentioned (d-1) ethylenic-unsaturated-carboxylic-acid unit, the same thing as above-mentioned (d) unsaturation carboxylic acid units is mentioned, and the rate in the copolymer X is preferably used at 0 to 1weight % of a rate zero to 2weight %. If it exceeds 2 weight %, the storage stability of the binder obtained, a water resisting property, and alkali resistance may get worse. As the above-mentioned (e-1) functional group content compound unit, the same thing as above-mentioned (e) functional group content compound unit is mentioned, and the rate in the copolymer X is preferably used at 0 to 1weight % of a rate zero to 2weight %. If it exceeds 2 weight %, the storage stability of the binder obtained, a water resisting property, and alkali resistance may get worse.

[0009]

As an aromatic vinyl unit in the above-mentioned copolymer Y portion (a-2), the same thing as above-mentioned (a) aromatic vinyl unit is mentioned. A rate in the copolymer Y of this (a-2) aromatic vinyl monomer unit is 35 to 75 weight % preferably 25 to 90weight %. In less than 25 weight %, if a copolymer may be sticky, intensity may be lost and it exceeds 90 weight %, it may be said that a copolymer becomes hard too much and bond strength and pliability as a binder are inferior. As the above-mentioned (b-2) conjugated diene unit, the same thing as above-mentioned (b) conjugated diene unit is mentioned. A rate in the copolymer Y of this (b-2) conjugated diene unit is 30

or less weight % preferably 35 or less weight %. If it exceeds 35 weight %, a copolymer may cover activated carbon too much, internal resistance may go up, and the electric double layer capacitor characteristic may be inferior. As the above-mentioned (c-2) (meta) acrylic ester unit, the same thing as above-mentioned (c) (meta) acrylic ester unit is mentioned. A rate in the copolymer Y of this (c-2) (meta) acrylic ester unit is 20 to 35 weight % preferably 11 to 40 weight %. In less than 11 weight %, when a constituent for electric double layer capacitor electrodes is prepared using a binder obtained and it applies to current collection material, elasticity and intensity of a coat are inferior and it is not desirable. When it exceeds 40 weight %, the stability of a polymerization system of a specific copolymer is inferior, and adhesion as a binder, etc. fall, and it is not desirable. As the above-mentioned (d-2) ethylenic-unsaturated-carboxylic-acid unit, the same thing as above-mentioned (d) unsaturation carboxylic acid units is mentioned, and a rate in the copolymer Y is preferably used at 2 to 10 weight % of a rate 0.5 to 30 weight %. The stability of a binder obtained as it is less than 0.5 weight % worsens, and it is easy to generate a congelation, and inferior to mechanical and the chemical stability of a binder. On the other hand, when it exceeds 30 weight %, viscosity of a binder obtained becomes high too much, and is inferior to storage stability, a water resisting property, and alkali resistance. As the above-mentioned (e-2) functional group content compound unit, the same thing as above-mentioned (e) functional group content compound unit is mentioned, and a rate in the copolymer Y is 2 to 10 weight % preferably zero to 30 weight %. When it exceeds 30 weight %, viscosity of a binder obtained becomes high too much, and is inferior to storage stability, a water resisting property, and alkali resistance.

[0010]

The rate of the copolymer X in a specific copolymer (copolymer X+ copolymer Y) is 20 to 70 weight % still more preferably ten

to 80weight % preferably five to 90weight %. The bond strength to the activated carbon of the binder obtained as the rate of the copolymer X is less than 5 weight %, a charge collector, etc. may be insufficient, and it may become that in which the intensity of the binder which will be obtained if it exceeds 90 weight % is inferior. As for a specific copolymer, in this invention, it is preferred that the copolymers X are a core and the core shell structure whose copolymer Y is shell.

[0011]

The binder for electric double layer capacitor electrodes of this invention consists of a drainage system dispersing element of a specific copolymer. 120-600 nm is desirable still more preferred, and the mean particle diameter of the specific copolymer particles distributed in this drainage system dispersing element is 140-400 nm. In a specific copolymer, many internal resistance becomes it high that the mean particle diameter of specific copolymer particles is less than 120 nm about activated carbon too much. On the other hand, when it exceeds 600 nm, the stability of a specific copolymer is inferior, the adhesiveness of the binder obtained with a specific copolymer becomes scarce, and the adhesive property to the current collection material of activated carbon is inferior. The solids concentration of the water dispersing element of a specific copolymer is usually 35 to 60 weight % preferably 20 to 65weight %.

[0012]

In this invention, a specific copolymer can be manufactured by carrying out the emulsion polymerization of the monomer which has the above-mentioned structural unit. A core consists of a copolymer whose glass transition point is -50-50 ** especially, and shell a specific copolymer of core shell structure which consists of a copolymer whose glass transition point is 0-100 **, Under existence of seed particles which a glass transition point becomes from a copolymer which is -50-50 **, A method of

carrying out seed polymerization of the monomer from which a glass transition point of the copolymer will be 0-100 ** is preferred, and, specifically, a method of polymerizing a monomeric mixture which gives the above-mentioned copolymer Y is preferred under existence of seed particles which consist of the above-mentioned copolymer X. Here, the usual emulsion polymerization is used for both manufactures and seed polymerization of seed particles. A publicly known method can be adopted on the occasion of the above-mentioned emulsion polymerization, and it can manufacture using an emulsifier, a polymerization initiator, a molecular weight modifier, etc. in an aqueous medium. Here, as an emulsifier, an anionic surface-active agent, a nonionic surface-active agent, an ampholytic surface active agent, etc. are independent, or two or more sorts can be used together and used. As an anionic surface-active agent, sulfate ester of higher alcohol, alkylbenzene sulfonates, an aliphatic-sulfonic-acid salt, sulfate ester of a polyethylene glycol alkyl ether, etc. are mentioned, for example. As a nonionic surface active agent, an alkyl ester type of the usual polyethylene glycol, an alkyl ether type, an alkylphenyl ether type, etc. are used. As an ampholytic surface active agent, as an anion portion, carboxylate, sulfuric ester salt, A sulfonate and a phosphoric ester salt are mentioned by what has amine salt and quaternary ammonium salt as a cation portion, and then specifically, Betaines, such as a lauryl betaine and a stearyl betaine; a thing amino acid type [, such as lauryl beta-alanine, stearyl beta-alanine, a RAURIRUJI (aminoethyl) glycine, and an OKUCHIRUJI (aminoethyl) glycine] etc. are used. The amount of emulsifier used in a polymerization of a specific copolymer is 0.5 to 5 weight section preferably to total monomer 100 weight section.

[0013]

As the above-mentioned polymerization initiator, water soluble polymerization initiator; benzoyl peroxide, such as sodium

persulfate, potassium persulfate, and ammonium persulfate, Oil soluble polymerization initiators, such as lauryl peroxide and 2,2'-azobis isobutylnitril; a redox system polymerization initiator by combination with a reducing agent, etc. are independent respectively, or can combine and use it. The amount of polymerization initiator used is 0.5 to 3 weight section preferably to total monomer 100 weight section. In a polymerization of a specific copolymer, a molecular weight modifier, a chelating agent, an inorganic electrolyte, etc. can use a publicly known thing. As the above-mentioned molecular weight modifier, halogenated hydrocarbon; n-hexyl mercaptan, such as chloroform and carbon tetrabromide, N-octyl mercaptan, n-dodecyl mercaptan, t-dodecyl mercaptan, Mercaptans, such as thioglycolic acid; all usable things can be used by the usual emulsion polymerizations, such as xantho gene; TAPINOREN, such as dimethyl xantho gene disulfide and diisopropyl xantho GENJI sulfide, and a alpha-methylstyrene dimer. The amount of molecular weight modifier used is usually five or less weight sections to total monomer 100 weight section.

[0014]

As a polymerization method of a specific copolymer which has core shell structure, ** After polymerizing the copolymer X with another polymerization vessel beforehand and adding the specified quantity to a polymerization vessel by making this copolymer X into seed particles, A method of polymerizing a method of polymerizing a monomer which gives the copolymer Y, or the ** copolymer X, and polymerizing a monomer which gives the copolymer Y within the same polymerization vessel, etc. are mentioned. Also in which method, polymerization conversion of the copolymer X is 70 weight % or more preferably 50weight % or more. As a method of preparing a monomeric mixture which gives the copolymer Y, ** After polymerizing in some of methods of preparing a monomeric mixture by whole-quantity package, and polymerizing, and ** monomeric mixtures, a method of adding the remainder continuously or intermittently or a method of adding

** monomeric mixture continuously from the start of a polymerization can be taken. These methods of teaching are also combinable. When usually polymerizing the copolymer X and polymerization temperature polymerizes 5-50 ** and the copolymer part Y preferably 5-80 **, it is 20-60 ** preferably 20-80 **. Polymerization time is usually 10 to 30 hours.

[0015]

<constituent for electric double layer capacitor electrodes> electric double layer capacitor electrode, After applying the current collection material dissolved on the electrode cloths obtained by making electrode cloths using the constituent for electrodes containing the activated carbon and the binder for electric double layer electrodes which become an electrode, it may dry and manufacture, and the above-mentioned constituent for electrodes can be applied to current collection material, and it can also dry and manufacture. As the above-mentioned activated carbon, there are powdered activated carbon, granulated active carbon, etc., and what processed this into fibrous or a solid state, and an activated-carbon-powder-like thing may be used. What processed into fiber cloths preferably the fibrous activated carbon which carbonized and carried out activation of the phenol resin is used. Conductive polymers, such as carbon; polyacethylenes, such as carbon black, Ketchen black, carbon fiber, mesophase carbon, and impalpable powder-like carbon, and Polly p-phenylene, etc. may be blended in order to give conductivity other than the above-mentioned activated carbon.

[0016]

In the above-mentioned constituent for electrodes, 0.5-10 weight-section combination of the binder of this invention is preferably carried out 0.1 to 20 weight section by solid content to activated carbon 100 weight section. Good adhesive strength [as opposed to / in the loadings of the binder of this invention / a moldability, a charge collector, etc. of activated carbon

at less than 0.1 weight sections] is not obtained, but if 20 weight sections are exceeded, excess voltage will go up remarkably, and it is ***** about an adverse effect to the electric double layer capacitor characteristic. 1-200 weight-section addition of the water soluble thickener may be carried out to specific copolymer 100 weight section at the constituent for electrodes using the binder of this invention if needed. As the above-mentioned water soluble thickener, carboxymethyl cellulose, methyl cellulose, hydroxymethylcellulose, ethyl cellulose, polyvinyl alcohol, polyacrylic acid (salt), oxidation starch, phosphorylation starch, casein, etc. are mentioned. As other ingredients, additive agents, such as nonionicoity as a stabilizing agent of dispersing agent; latex, such as sodium hexametaphosphate, sodium tripolyphosphate, sodium pyrophosphate, and sodium polyacrylate, and an anionic surface-active agent, may be added.

[0017]

As a coating method of the constituent for electric double layer capacitor electrodes produced by making it above, Arbitrary coater heads, such as the reverse roll method, the comma bar method, the GURABIYA method, and the air knife method, can be used, and neglect desiccation, an air blasting dryer, a drying-by-warm-air machine, an infrared heat machine, a far-infrared-heating machine, etc. can be used as a drying method. Drying temperature may usually be performed at around 150 **, and may carry out press and vacuum drying if needed. As current collection material used for an electric double layer capacitor electrode, platinum, aluminum, etc. are mentioned, for example. Current collection material may be used in the state of a metallic foil, may spray metal on the electrode cloths which consist of the above-mentioned constituent for electrodes by a plasma metal spray etc., and may form an electrode layer.

[0018]

<Electrode double layer capacitor>

When assembling an electric double layer capacitor using the electric double layer capacitor electrode produced by performing it above, as an electrolysis solution, For example, although ether, ketone, lactone, nitril, amines, amide, a sulfur compound, chlorinated hydrocarbon, ester species, carbonate, a nitro compound, a phosphoric ester system compound, a sulfolane system compound, etc. can be used, Ether, ketone, nitril, chlorinated hydrocarbon, carbonate, and a sulfolane system compound are especially preferred. As these examples of representation, a tetrahydrofuran, 2-methyltetrahydrofuran, 1,4-dioxane, an anisole, mono- glyme, acetonitrile, Propionitrile, 4-methyl-2-pentanone, butyronitrile, Valeronitrile, benzonitrile, 1,2-dichloroethane, gamma-butyrolactone, Dimethoxyethane, methyl formate, propylene carbonate, Although ethylene carbonate, dimethylformamide, dimethyl sulfoxide, a dimethylthioformamide, sulfolane, 3-methyl-sulfolane, trimethyl phosphate, phosphoric acid triethyl, these mixed solvents, etc. can be mentioned, It is not necessarily limited to these. If it requires, an electric double layer capacitor is constituted using parts, such as a separator, a terminal, and an electric insulating plate. Although not limited especially as a structure of an electric double layer capacitor, the wound type form which wound around rolled form a cathode, an anode, the coin type that comprised a separator when requiring further or the cathode, the anode, and the separator is mentioned as an example. The electric double layer capacitor manufactured using the binder for electric double layer capacitor electrodes of this invention can be used concretely conveniently for backup power supplies, such as AV equipment, OA equipment, and communication equipment.

[0019]

[Working example] An embodiment explains this invention in more detail below. However, this invention is not restrained at all by these embodiments. Each valuation method in an embodiment

and a comparative example is shown below.

(1) the evaluation of the binder for electric double layer capacitor electrodes

Measurement of particle diameter

Particle diameter was measured using measurement Otsuka Electronics Co., Ltd. make laser particle diameter analysis-system LPA-3000s/3100.

measurement of the glass transition point (T_g)

The drainage system dispersing element adjusted the pH to 8 with 0.5N ammonia solution was applied to the crow board, was dried at 120 °C for 1 hour, and the polymer film was obtained. This was used and it measured using the differential scanning calorimeter made from SEIKO Electronic industry.

(2) the evaluation of the electric double layer capacitor electrodes

Fibrous-activated-carbon (total specific surface area =1700m²/g) 100 weight section and binder 1 weight, as a thickening agent, carboxymethyl cellulose solution one weight section by solid content was added and mixed well, and the constituent for electric double layer capacitor electrodes was manufactured, it pressed so that it might be set to 1 mm in thickness with a hydraulic press, and vacuum drying was performed at 150 °C for 2 hours, and the electrode layer was produced. The following evaluations were performed using the obtained electrode layer.

the Clemens type of a product made from Intensity Tester Industry of an electrode -- "it scratched and film strength of an electrode layer was measured by hardness scale." A measuring method is JIS K5400. It carried out according to 8.4.1. Resistance of an electrode layer obtained by a measuring method 4 terminal method of internal resistance was measured.

(3) A constituent for electrodes obtained by the evaluation above (2) of an electric double layer capacitor was coated in a bar coating machine on 18-micrometer-thick platinum foil (coating surface product; 5 cm x 15 cm), and vacuum drying was performed at 150 °C for 2 hours. An electrolysis solution which

dissolved tetraethylammonium tetrafluoroborate in propylene carbonate was made to permeate what put a separator made from polyethylene by a hex TOSERA needs company between two electrodes obtained by piercing an obtained electrode plate to discoid 20 mm in diameter. An upper swine and a lower case were piled up on this, it sealed with packing, and a coin type electric double layer capacitor was produced. It discharged by the 1-mA constant current per 1F to this coin type electric double layer capacitor, and electric capacity was measured.

[0020]

70 copies of ion exchange water and 0.3 copy of potassium persulfate were taught to autoclave provided with one to embodiment 4 agitator, respectively, nitrogen gas replaced a gas phase portion for 15 minutes, and temperature up was carried out to 80 **. On the other hand, an ingredient shown in Table 1 with another container was mixed, and it was dropped at said autoclave over 15 hours. During dropping, it reacted at 80 **. A reaction was terminated after agitating at 85 more ** for 5 hours, after an end of dropping, and. A potassium hydrate adjusted pH to seven after cooling at 25 **, steam was introduced after that, a remains monomer was removed, and a binder for electric double layer capacitor electrodes of this invention which subsequently condenses and consists of a water dispersing element of a specific copolymer was obtained. An evaluation result is shown in Table 3.

Have a polymerization agitator of Embodiments 5 and 6 (1) copolymer X, and in the possible autoclave of temperature control 200 copies of water, 0.5 copy of sodium dodecylbenzenesulfonate, 1.0 copy of potassium persulfate, Taught collectively the monomer component which gives the molecular weight modifier and copolymer X portion which were shown in 0.5 copy of sodium bisulfite, and Table 1, and it was made to react at 45 ** for 6 hours, and checked that polymerization conversion was not less than 70%.

(2) Continue after the polymerization of the polymerization

above (1) of the copolymer Y, add continuously the mixture of the monomer component which gives the molecular weight modifier and the copolymer Y which were shown in Table 1 over 7 hours at 60 **, and a polymerization is made to continue. It was made to react at 70 ** over 6 hours after the end of continuation addition, and the binder for electric double layer capacitor electrodes of this invention which consists of a water dispersing element of a specific copolymer was obtained. Final polymerization conversion was 98 to 99%. It evaluated using each of the obtained binder for electric double layer capacitor electrodes. An evaluation result is shown in Table 3 and 4. In one to comparative example 4 Embodiment 1, the binder for electric double layer capacitor electrodes which consists of a water dispersing element of a polymer like Embodiment 1 was obtained except having carried out the presentation of the monomer component as in Table 2. An evaluation result is shown in Table 3.

[0021]

[Table 1]

実施例	1	2	3	4	5		6	
X/Y各成分比	—	—	—	—	X	Y	X	Y
ST					33	65	40	56
BD					36	10	29	13
MMA					30	18	18	20
BA					—	4	12	6
AA					—	1	—	2
IA					1	2	1	1
N-MAM					—	—	—	2
α -MSD					0.1	0.2	0.1	0.2
t-DM					0.2	0.1	0.1	0.1
Tg (°C)					0	59	-3	46
全体の成分比								
ST	47	48	62	71	49		48	
BD	39	36	21	14	23		21	
MMA	10	12	12	12	24		19	
BA	—	—	—	—	—		9	
AA	—	1	1	1	2		1	
IA	4	3	2	2	0.5		1	
N-MAM	—	—	2	—	1.5		1	
α -MSD	—	—	—	—	0.15		0.15	
t-DM	—	—	—	—	0.15		0.1	
平均粒径(nm)	150	200	150	240	160		150	
全体のTg(°C)	-10	-5	30	55	27		20	

[0022]

[Table 2]

比較例	1	2	3	4
共重合体成分				
ST	73	20	60	29
BD	25	68	25	59
MMA	—	9	15	10
IA	2	3	—	2
平均粒径(nm)	155	100	130	80
全体の Tg(°C)	-5	30	23	-41

[0023]

The cable address of the monomer in Tables 1 and 2 shows the following compound.

ST= styrene ((a) ingredient)

BD= butadiene ((b) ingredient)

MMA= methyl methacrylate ((c) ingredient)

BA= butyl acrylate ((c) ingredient)

AA= acrylic acid ((d) ingredient)

IA= itaconic acid ((d) ingredient)

N-MAM=N-methylolacrylamide ((e) ingredient)

Alpha-MSD = alpha-methylstyrene dimer (molecular weight modifier)

t-DM=t-dodecyl mercaptan (molecular weight modifier)

[0024]

[Table 3]

	電極強度(gf)	内部抵抗(m Ω/cm)	静電容量(F/g)
実施例 1	100	35	20
実施例 2	100	30	25
実施例 3	130	24	20
実施例 4	150	18	19
実施例 5	150	16	21
実施例 6	140	22	21
比較例 1	60	45	12
比較例 2	80	50	10
比較例 3	50	38	15
比較例 4	55	67	7

[0025]

Embodiments 1-5 of Table 1 are the copolymers of the range of this invention, and Table 2 is a presentation and T_g of the copolymer besides the range of this invention, and mean particle diameter. When the copolymer of this invention is used so that clearly from Table 3, it excels in the balance of the electrode strength of an electric double layer capacitor electrode, internal resistance, and also the electric capacity of an electric double layer capacitor. On the other hand, the comparative example 1 is an example of the copolymer which does not include an acrylic ester (meta) unit.

Electrode strength and internal resistance are inferior and the electric capacity of an electric double layer capacitor is low. The conjugated diene monomeric unit of the comparative example 2 is an example of the copolymer besides the range of this invention.

Internal resistance is high and the electric capacity of an electric double layer capacitor is low.

The comparative example 3 is an example of the copolymer which does not include a functional group content compound unit.

It is inferior to binder performance, electrode strength is inferior, and the electric capacity of an electric double layer capacitor is low.

A conjugated diene monomeric unit and Tg of the comparative example 4 are the examples of the copolymer besides the range of this invention.

Electrode strength and internal resistance are inferior and the electric capacity of an electric double layer capacitor is low.

[0026]

[Effect of the Invention] which the binder for electric double layer capacitor electrodes of this invention can produce the electrode which activated carbon bound strongly to the charge collector, and can attain high-capacity-izing of an electric double layer capacitor, and the good large discharge current characteristic.

[Translation done.]